

ISSN 0825-4591

PROCEEDINGS

ENVIRONMENTAL RESEARCH:
1989 TECHNOLOGY TRANSFER CONFERENCE

November 20 & 21, 1989

Royal York Hotel

Toronto, Ontario

VOLUME I

FEATURE PRESENTATIONS

AIR QUALITY RESEARCH

WATER QUALITY RESEARCH

Sponsored by
Research and Technology Branch
Environment Ontario
Ontario, Canada

ABWB

A4 DEVELOPMENT OF AMBIENT AIR MONITORING METHODOLOGIES FOR

DIOXINS AND FURANS

P. Steer, R. Clement, C. Tashiro and M. Lusic
Ontario Ministry of the Environment
Toronto, Ontario, CANADA M5S 1Z8

T. Dann, C. Chiu and M. Bumbaco
Environment Canada
Ottawa, Ontario, CANADA K1A 0H3

ABSTRACT

This program began in 1987 in recognition of the high public profile of dioxins and furans in the environment and the lack of an ambient air reference method for these compounds. Objectives of the work were to standardize sampling and analytical methods applicable to the determination of trace levels of dioxins and furans in ambient air; to document method performance; to assess the ability of commercial laboratories to successfully apply developed analytical procedures; and to develop a data base for dioxins and furans in ambient air. Results of ambient air monitoring for dioxins and furans carried out in Ontario are discussed. Results from an inter-laboratory round robin analytical methodology evaluation are also presented.

INTRODUCTION

Development of ambient air monitoring methodologies for polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs and PCDFs) began in 1987 with direction from the Canadian Council of Resource and Environment Ministers' (now the Canadian Council of Environment Ministers) Working Group on Monitoring of Airborne Substances Excluding SO₂ and NO_x. A three-year program was outlined to allow completion of a national reference method for dioxins and furans in ambient air, to determine the capability of Canadian laboratories to analyze these samples, and to transfer the technology to provincial, municipal, university, and private organizations.

The first part of this paper examines ambient levels of dioxins and furans measured at four sites in southwestern Ontario (Figure 1). Two sites (Windsor and Walpole Island) are operated under the auspices of the Environmental Protection Service of Environment Canada (EC) as part of the Detroit Incinerator Monitoring Program (Environment Canada, 1989). The Air Resources Branch of the Ontario Ministry of the Environment (MOE) also has a sampler at Windsor and operates two additional sites; one on Toronto Island as part of the Toronto Waterfront Remedial Action Plan, and the other in Dorset as a background site and for sampler development work.

In the second part of this paper, results of an inter-laboratory analytical method comparison are presented. Ambient air samples for this round robin study were collected at the Windsor site.

AMBIENT AIR LEVELS

A modified high volume sampler was used to draw air through a teflon-coated glass fibre filter upstream of a polyurethane foam (PUF) vapour trap. Sampling times varied between 24 hr and 72 hr yielding sampled volumes of 500 m³ to 2000 m³. Exposed samples were spiked with ¹⁴C₁₂-labelled PCDD surrogates and Soxhlet extracted with toluene. The extract was concentrated by rotary evaporation and worked up using a modified Dow clean-up. Samples were analyzed by GC/MS/MS on a Finnigan TSQ70 (MOE) or a Finnigan 4500 HRGC/LRMS (EC). Specific details of the sampling and analytical methodologies have been reported elsewhere (Tashiro, et al, 1989; Dann, et al, 1988).

There are no national air quality objectives for PCDDs or PCDFs, however, Ontario has a provisional ambient air guideline for 2,3,7,8-TCDD of 30 pg/m³ annual average. Average values of T₄CDD, T₄CDF, total CDD, and total CDF from four sites in Southwestern Ontario are given in Table 1.

TABLE 1: Average Concentrations (pg/m³) of Tetra and Total Dioxins and Furans From Four Sites in Southwestern Ontario.

WINDSOR (EC)						WALPOLE ISLAND					
	\bar{x}	s.d.	max	min	n		\bar{x}	s.d.	max	min	n
T ₄ CDD	—	—	ND	ND	13	T ₄ CDD	—	—	ND	ND	7
T ₄ CDF	0.2	0.2	0.8	ND	13	T ₄ CDF	0.1 ¹	—	0.1	ND	7
Total CDD	2	2	7	0.4	13	Total CDD	0.5	0.4	1	ND	7
Total CDF	0.4	0.4	1	ND	13	Total CDF	0.1 ¹	—	0.1	ND	7
WINDSOR (MOE)						DORSET					
	\bar{x}	s.d.	max	min	n		\bar{x}	s.d.	max	min	n
T ₄ CDD	0.5	0.4	1	0.09	6	T ₄ CDD	0.1	0.05	0.2	0.08	5
T ₄ CDF	0.7	0.3	1	0.3	6	T ₄ CDF	0.2	0.1	0.3	0.02	5
Total CDD	4	4	11	1	6	Total CDD	2	4	9	0.2	5
Total CDF	2	1	4	1	6	Total CDF	0.9	1	3	0.06	5
TORONTO ISLAND						NOTES:					
	\bar{x}	s.d.	max	min	n	All results to one significant figure					
T ₄ CDD	0.2	0.2	0.5	0.05	5	¹ Only one positive result					
T ₄ CDF	0.4	0.4	1	0.02	5	ND = Not Detected					
Total CDD	2	1	4	0.9	5	Windsor (EC) 87+08 to 88+10					
Total CDF	1	1	3	0.4	5	Windsor (MOE) 88+08 to 89+01					

Of seven samples collected at Walpole Island, T₄CDD was not detected in any samples and only one sample yielded a positive result for T₄CDF and total CDF. Of the maximum values for total CDD reported for Windsor (MOE) and Dorset, O₄CDD accounts for 9 and 7 pg/m³ respectively. The amount of T₄CDD and T₄CDF relative to total CDD and total CDF is shown in Figure 2. If the 2,3,7,8-substituted isomer accounted for all of the TCDD measured, ambient air levels at the sites sampled are well below the provincial provisional guideline.

Results reported here for Ontario are comparable to ambient air levels measured elsewhere in North America (e.g. Hunt and Maisel, 1989; Smith et al, 1989; Eitzer and Hites, 1987).

INTER-LABORATORY COMPARISON

Having established sampling protocols for dioxins and furans in air (Dann et al, 1988), the next stage was to determine the capability of private laboratories to analyze ambient air samples. Collocated samplers were installed at the Windsor site and ambient air samples were collected for analysis by each laboratory. Participating laboratories received the following: i) an exposed teflon-coated glass fibre filter (GFF) and polyurethane foam (PUF) plug; ii) a spiked extract consisting of combined extracts from collocated samplers; iii) a blank GFF and PUF plug; iv) a low level spiked blank (TCDD, HxCDD and OCDD spiked at 12, 20, and 29 pg/ μ L respectively) and iv) an unknown standard mixture. Laboratories were instructed to use their own methodologies.

The laboratories participating in the study included: Ontario Ministry of the Environment; Environment Canada; ELI ECO Laboratories; Novalab Limited; Mann Testing Laboratories; Wellington Environmental Consultants; and Zenon Environmental Laboratories. The laboratories have been given random numbers for the intercomparison. A comparison of the clean-up and analysis methods used by the various laboratories is shown below in Table 2.

TABLE 2: Comparison of Clean-Up and Analysis Methods Used by Participating Laboratories.

	MOE	ENVIRONMENT CANADA	ELI ECO	MANN	NOVALAB	WELLINGTON	ZENON
CLEAN-UP							
a. Extraction	Soxhlet -toluene	Soxhlet -toluene	Soxhlet -toluene	Soxhlet -toluene	Soxhlet -toluene	Soxhlet -toluene	Soxhlet -CH ₂ Cl ₂
b. Column Clean-up	Modified silica Alumina	Modified silica Alumina	Modified silica Alumina	Modified silica Alumina	Modified silica Alumina	Modified silica Alumina	Modified silica Alumina
c. Carbon Clean-up	none	none	Carbon on glass fibre	none	Carbopack C on Celite	none	none
ANALYSIS							
a. GC-MS	Finn TSQ70	Finn 4500	HP5970 MSD	Finn 4500	HP5970 MSD	VG 12000	Finn TSQ70
b. Final Volume (μ L)	10	20	20	50	10	10	25
c. Injection Volume (μ L)	2	2	2	2.5	2	2	1
d. Surrogates used (¹⁴ C ₁₂)	TCDD PCDD HxCDD HpCDD OCDD	TCDD PCDD HxCDD HpCDD OCDD	TCDD PCDD HxCDD HpCDD OCDD	TCDD OCDD	TCDD OCDD	TCDD PCDD HxCDD HpCDD OCDD	TCDD HxCDD OCDD
e. Peak Height or Area	area	area	area	area	area	height	area

Results from the exposed filter and PUF analysis and the spiked combined extract analysis are shown in Figures 3 and 4 respectively. For both analyses, there is considerable between-lab variability. When positives were detected, the number of isomers reported also varied from lab to lab. Some of the laboratories did not detect the spikes that had been added to the combined extract.

Results from the low level spiked blank are more consistent, with the exception of lab #3 not detecting the HxCDD spike. For the tetra-, hexa-, and octa- CDD congeners at respective spike levels of 12, 20, and 29 pg/ μ L, the average levels

reported were; tetra: 11 ± 4 ; hexa: 16 ± 4 and; octa: 25 ± 10 .

Reasonably consistent results were also obtained from analysis of the unknown standard mixture (Table 3). Some laboratories had trouble with certain congeners and overall standard deviations were larger for the higher chlorinated congeners.

TABLE 3: Analysis of an Unknown Standard Mixture (Concentrations in $\text{pg}/\mu\text{L}$).

LABORATORY	1	2	3	4	5	6	7	EXPECTED VALUES	AVERAGE
Congener									
TCDD	87	81	136	113	100	160	101	100	111 ± 28
PCDD	89	80	132	73	66	95	92	100	90 ± 21
HxCDD	180	170	189	89	130	170	151	160	154 ± 35
HpCDD	82	110	141	99	130	100	107	200	110 ± 20
OCDD	200	190	227	100	190	200	189	200	185 ± 40
TCDF	39	39	51	40	68	45	42	50	46 ± 11
PCDF	46	41	58	37	51	59	41	50	48 ± 9
HxCDF	71	72	102	61	100	98	72	80	82 ± 17
HpCDF	98	78	100	70	200	80	93	100	94 ± 57
OCDF	84	79	110	46	134	140	83	100	97 ± 33

Five of seven laboratories demonstrated capability for the analysis of dioxins and furans in ambient air, however, further analytical methodology development is required by all laboratories as evidenced by variable results from both the exposed sample and the spiked extract analysis.

CONCLUSIONS AND RECOMMENDATIONS

Levels of dioxins and furans in ambient air in Ontario are typical of those reported in the literature for other localities in North America. Analytical methodologies for ambient air samples need to be refined and the effect of sample to sample variation from collocated samplers should be investigated. A second inter-laboratory round robin with replicate samples is recommended.

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FIGURE 1: Dioxin and Furan Ambient Air Monitoring Locations.



FIGURE 2: Average Ambient Levels of Dioxins and Furans at Selected Sites in Ontario

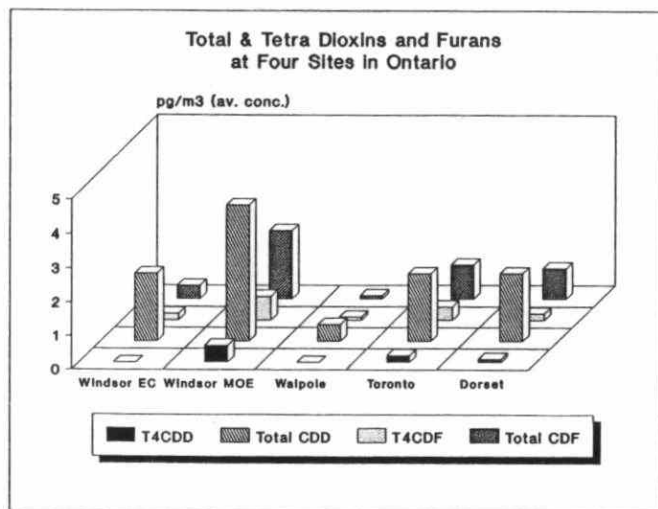


FIGURE 3: Round Robin Analytical Results: Exposed Filter and PUF Plug Analysis

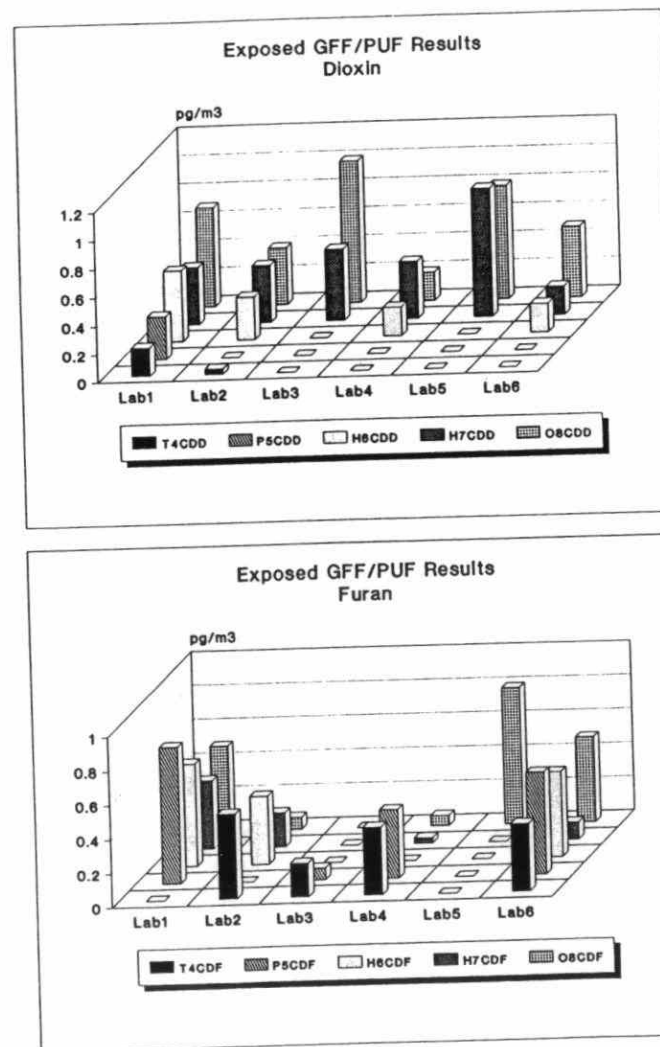
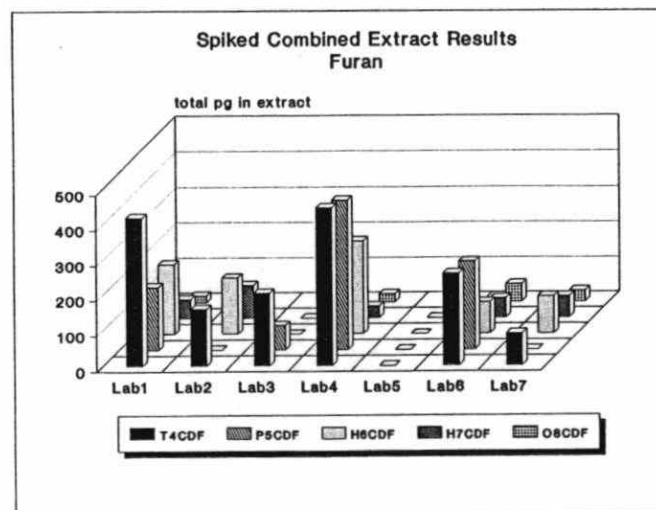
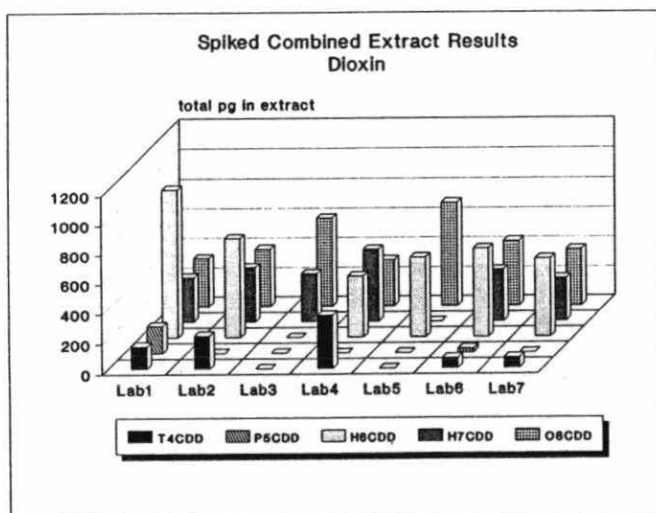


FIGURE 4: Round Robin Analytical Results: Spiked
Combined Extract Analysis





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TD/5/T43